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TITLE: DEVELOPMENT OF THE VLS PROCESS FOR SiC WHISKER GROWTH

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DEVELOPMENT OF THE VLS PROCESS FOR SiC WHISKER GROWTH*

PRESENTED BY

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I would like to begin by acknowledging my colleagues whose results are represented in the following, and who have helped in putting this presentation together. These investigators are listed in Fig. 1.

Fig. 2 outlines the organization of the whisker development program at Los Alamos. Sample quantities of whiskers are required for ceramic matrix composite work and for supply of material used in whisker characterization. Process modelling studies are being conducted, following the day-to-day operation of the furnace used for preparation of these samples.

Extensive work is underway to characterize the starting properties of the SiC whiskers, and the effect of subsequent processing on their strength. An important element of our work is that devoted to process scaleup. This latter work is focused on developing a fundamental understanding of the VLS process as it is related to this particular material.

The objectives of our ceramic matrix composites work are given in Fig. 3. High modulus fibers stiffen lower modulus ceramics and also provide strengthening through load transfer. (Fig. 4). Major improvements in fracture toughness as the result of crack deflection and/or fiber pull-out are also expected from this approach. Investigations are being carried out on glass-matrix and hot-pressed silicon nitride matrix composites and planned for reaction-bonded silicon nitride composites.

Fig. 5 shows the objectives and approaches of the SiC whisker modelling studies. Right now we are looking at flow parameters such as the Reynold's Number (N_{RE}) and the Grashoff Number (N_{GR}) to see if the growth rate per unit area can be correlated with either of these. In addition we model the chemical composition of the gases, growth temperature, and geometrical effects on growth rate, and the morphology of the product. Fig. 6 shows the effect of total gas flow, for one reactor geometry, on growth rate. This trend was not always observed when the geometry varied.

Fig. 7 summarizes measurements of whisker strength as a function of length. The interesting result is that length has little effect above a gauge length of $\sim$ 5 mm. The low value of Weibull Modulus is a measure of the scatter in the values of strength.

We are beginning some work to characterize the microstructure of as-grown whiskers. John Porter of USC has made a preliminary examination of some of the whisker types in the high voltage TEM at Berkeley. Typical micrographs of one of the needle types are shown in Fig 8. Characteristic features are the longitudinal lines which appear to be dislocations, possibly partial dislocations, as well as less typical inclined features which may also be dislocations. The objective of this work is to investigate the grown-in substructure, and to look for features which may be strength-limiting.

A series of experiments underway to investigate the effect of handling on whisker properties is shown in Fig. 9. This series addresses the possibility of damage which would occur in both whisker and composite processing operations.

Additional processing and environmental concerns are discussed in Fig. 10. Current procedure is to etch whiskers after harvesting to remove the metal catalyst balls which are concomitant to the VLS process. Strength tests before and after etching have shown a mild strength reduction which may be related to chevron-like features which appear on the whisker surface. In addition, preliminary results have suggested a reduction of strength after elevated temperature anneal. However, examination of these whiskers have subsequently shown evidence of appendages associated with the break, hence suggesting the possibility that whiskers sintered or interacted with other whiskers or impurities, thus accounting for the loss of strength.

The problem areas in the present process include low yields, mixed whisker types, non-optimum reproducibility, and incomplete understanding of the process variables which affect these other deficiencies. Clearly, then, the route to scaling of the process must begin by carefully investigating the role of process variables in the yield, whisker morphology, and process reproducibility. As given in Fig. 11, this work is beginning by addressing the source materials and what we have termed "catalyst phenomenology."

Figs. 12 and 13 show a series of reactions now used to give SiC as well as some alternative sources to give the same product. Thermodynamically, $SiCl_4$, Si_{H4}, and CH_3SiCl_3 are suited to the production of Si. Additionally, $SiCl_3$ is available at low cost. The principal objective here is to see if we can independently and directly control the gas composition, and by so-doing, improve the yield.

"Catalyst phenomenology" describes a series of experiments being carried out to examine the relationship of the catalyst to the growth process, as shown in Fig. 14. Unknowns to be addressed include the following. An incubation time for whisker growth is apparent from past work with this process. This may result from operation of the Si source, the time for saturation of the catalyst balls or from some other effect. Study of nucleation events is important since it may be a route to more efficient conversion of catalyst-balls to whiskers. Evidence for the importance of impurities on growth is available but indefinite. This subject may have importance in controlling quality in manufacturing. The whisker growth rate is not known, nor is the effect of process variables on this rate understood. Whiskers of lengths differing by 10 times result from similar runs. Finally, although a definite size relationship is expected between the whisker diameter and the size of the catalyst ball from which it grows, we have no quantitative comfirmation of this. Once again, impurity effects may be very important here.

In summary, our whisker work involves preparation of whisker samples, whisker characterization, and process scaleup. Sample whiskers are used for composite preparation and for whisker characterization work, while modelling of the production process is itself proving useful. The approach to scaleup recognizes the importance of a full understanding of the process variables. Hence our work in this area is proceeding with studies of the chemistry of the process gases and investigation of the growth mechanism.

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W. J. PARKINSON

Figure 1

THE LOS ALAMOS WHISKER WORK INCLUDES ELEMENTS DEVOTED TO WHISKER SAMPLE PREPARATION, CHARACTERIZATION, AND PROCESS DEVELOPMENT AND SCALEUP

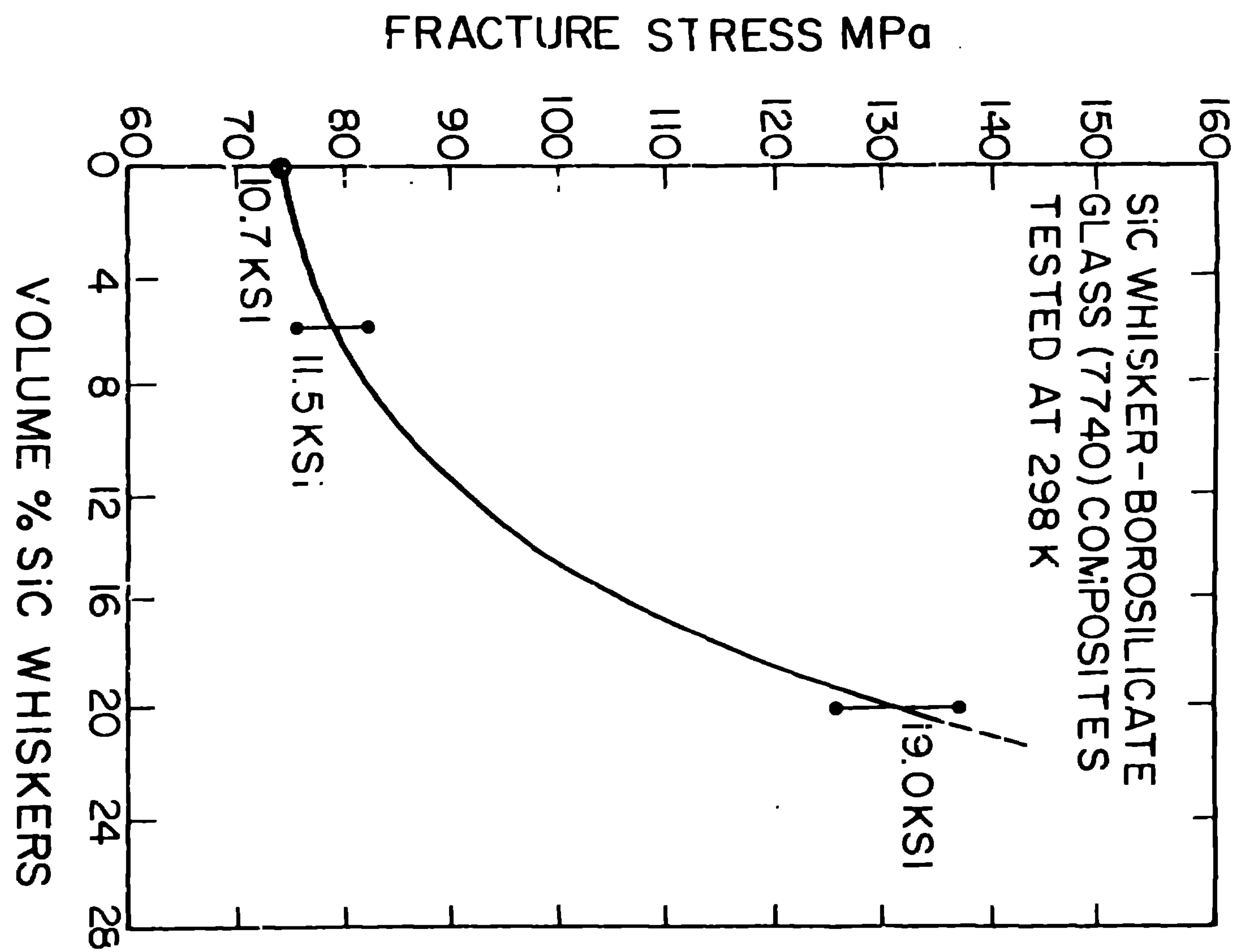
	COMPOSITES
SAMPLES:	CHARACTERIZATION
	MODELLING
	STRENGTH
CHARACTERIZATION:	HANDLING
	ENVIRONMENT
SCALEUP:	MECHANISM OF GROWTH
	ROLE OF: SOURCE MATERIALS
	CATALYST
	SUBSTRATE
	CONFIGURATION

Figure 2

THE OBJECTIVE OF OUR COMPOSITES WORK IS TO DEVELOP STRONG, HIGH FRACTURE TOUGHNESS CERAMICS

1. GLASS-MATRIX
2. HPSN
3. RBSN

Figure 3



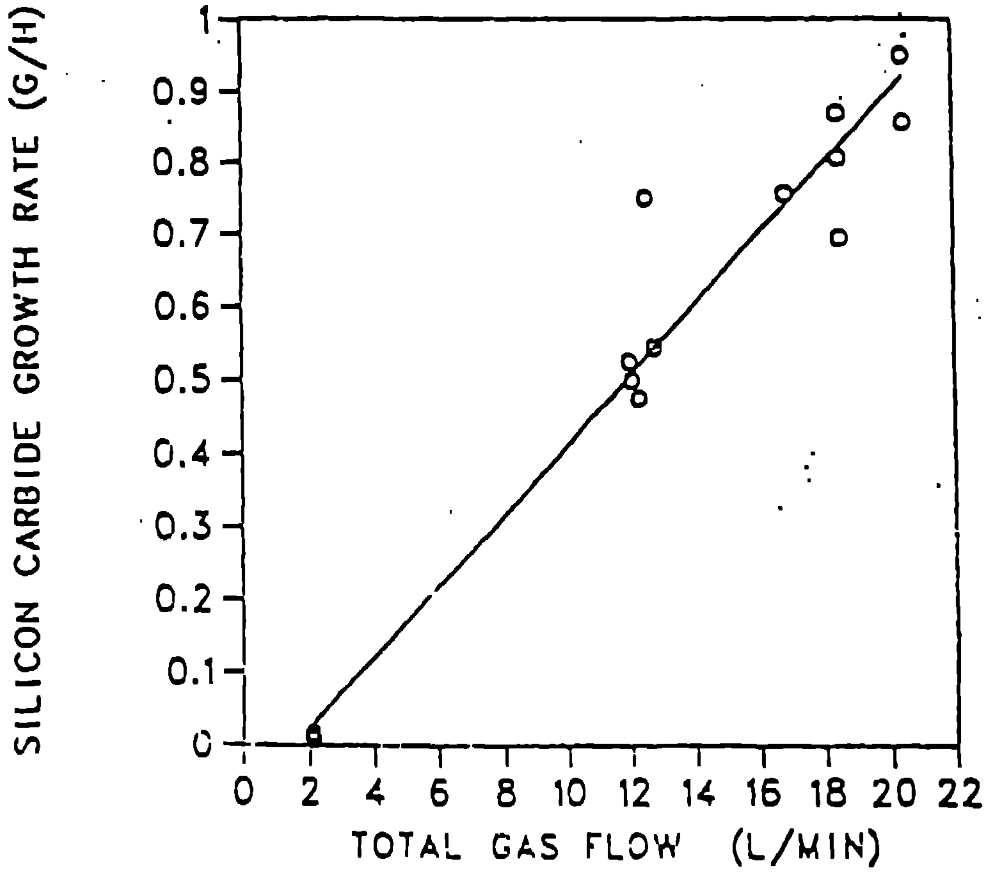
FRACTURE STRESS MPa
SiC WHISKER-BOROSILICATE
GLASS (7740) COMPOSITES
TESTED AT 298 K
10.7 KSI
11.5 KSI
19.0 KSI
VOLUME % SiC WHISKERS

Figure 4

THE OBJECTIVES OF THE CURRENT MODELLING WORK ARE TO ESTABLISH THE ROLE OF VARIABLES ON WHISKER QUANTITY AND QUALITY

- Growth Rate as F (N_{RE})
- Growth Rate as F (SiO Loss)
- Growth Rate as F (T)
- Other Variables
- Wool vs Needles

Figure 5



Total flow vs SiC growth rate

Figure 6

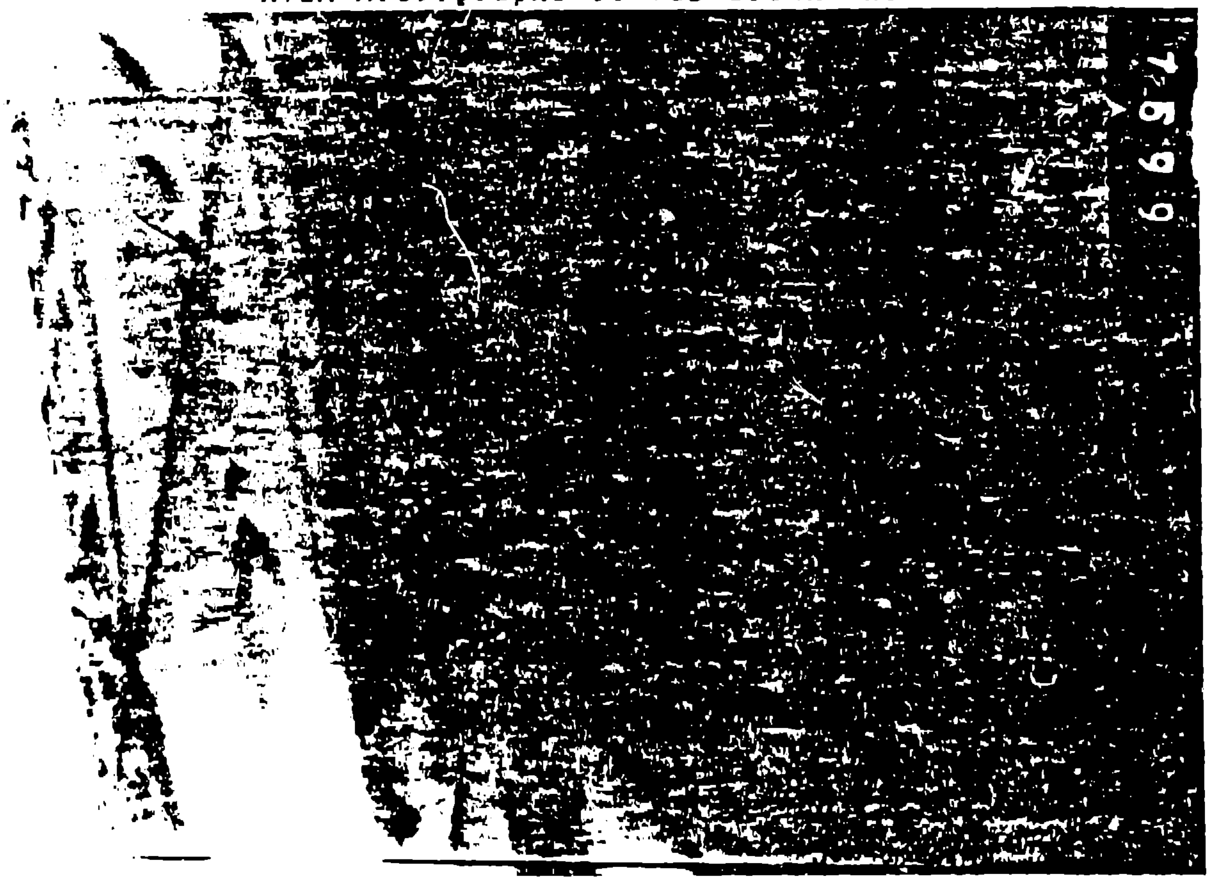
WHISKER STRENGTH HAS BEEN CHARACTERIZED AS A FUNCTION OF LENGTH

$\bar{\sigma}$ = 1.2 MPSI, 5 MM $\leq$ L $\leq$ 20 MM
$\bar{\sigma}$ = 2.2 MPSI, L $<$ 5 MM

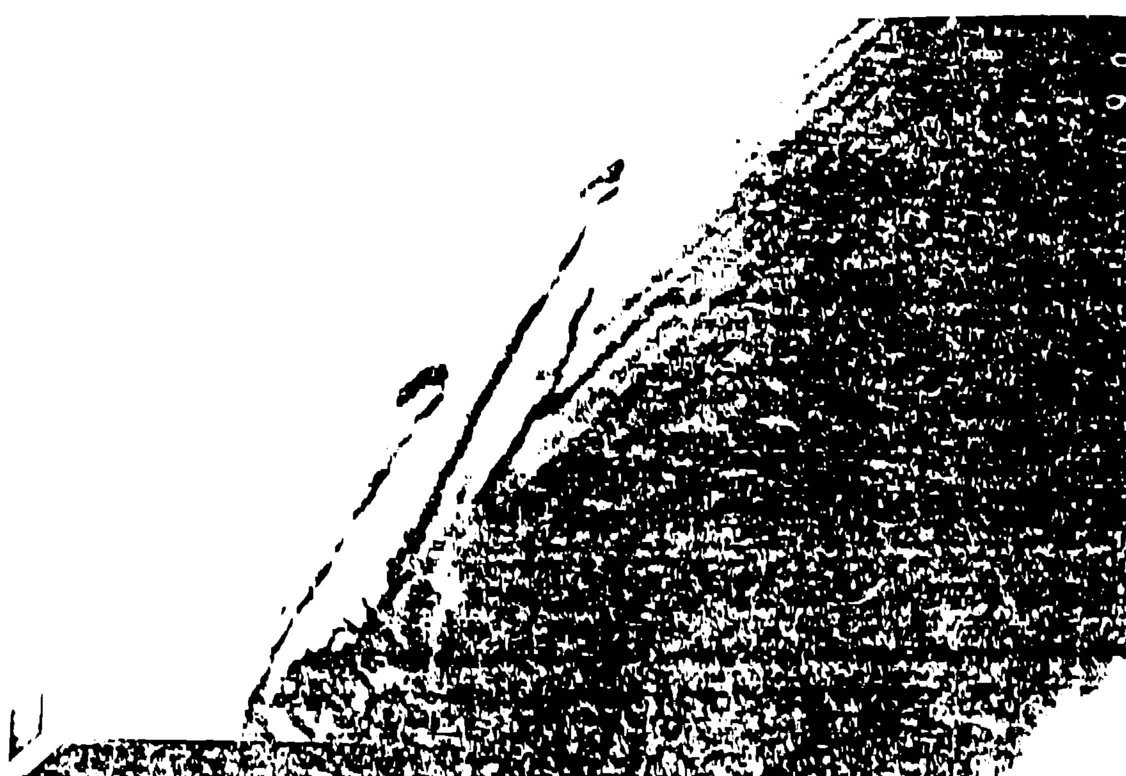
WEIBULL MODULUS = 2.7

Figure 7

HVEM Micrographs of VLS Grown Whiskers



Specimen 6A. Fiber 1. Magnification: 40K 7699
Longditudinal and angled dislocations.



Specimen 6A. Fiber 2. Magnification 20K 6699
Two sets of Dislocations.

Figure 8

EFFECT OF HANDLING ON WHISKER PROPERTIES IS NOT KNOWN

PROBLEM IS BEING ADDRESSED THROUGH TESTS ON:

1. VIRGIN-COATED WHISKERS
2. VIRGIN-UNCOATED WHISKERS
3. HARVESTED WHISKERS
4. PROCESSED WHISKERS

Figure 9

EFFECT OF ENVIRONMENT AND OTHER PROCESSING STEPS IS IMPORTANT SINCE THESE ARE FACTORS IN COMPOSITES TECHNOLOGY

1. ETCHING (REMOVE CATALYST, SURFACE COATING)
   CHEVRON NOTCHES
   STRENGTH REDUCTION

2. ELEVATED TEMPERATURE SOAK
   REDUCED STRENGTH OBSERVED
   BUT RESULTS INCOMPLETE

Figure 10

THE ROLE OF ALL OF THE PROCESS VARIABLES MUST BE UNDERSTOOD QUANTITATIVELY IN ORDER TO DEVELOP A HIGH-YIELD MANUFACTURING PROCESS

WORK IS FOCUSSING ON:

- ALTERNATE SOURCE MATERIALS
- CATALYST PHENOMENOLOGY

Figure 11

SiC WHISKERS CAN BE MADE FROM SAND AND METHANE

$$C + SiO_2 \xrightarrow{H_2} CO(G) + SiO\ (G)$$
$$CH_4 \longrightarrow C + 2H_2$$
$$SiO + C \longrightarrow Si + CO$$
$$C + Si \longrightarrow SiC$$

OF THESE REACTIONS, THE FIRST IS EXPERIMENTALLY DIFFICULT TO CONTROL

Figure 12

ALTERNATE SI SOURCES APPEAR TO BE MORE

1. $SiH_4 \longrightarrow Si + 2H_2$
2. $SiCl_4 + 2H_2 \longrightarrow Si + 4HCl$
3. $CH_3SiCl_3 \longrightarrow SiC + 3HCl$

Figure 13

STUDY OF CATALYST PHENOMENOLOGY AIMS TO ESTABLISH A PICTURE
OF THE SUBSTRATE - WHISKER - CATALYST COMPOSITE

IMPORTANT ASPECTS INCLUDE:

1. RATE LIMITING STEP
2. NUCLEATION EVENTS
3. IMPURITY EFFECTS
4. GROWTH RATE
5. SIZE - RELATIONSHIP

Figure 14